

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 716 882 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
19.06.1996 Bulletin 1996/25

(51) Int Cl.⁶: B01J 20/26, C08F 8/30

(21) Application number: 95307835.9

(22) Date of filing: 02.11.1995

(84) Designated Contracting States:
DE FR GB

• Yamamoto, Yoko
Okayama-shi, Okayama-ken (JP)

(30) Priority: 13.12.1994 JP 333141/94

(74) Representative: Gaunt, Robert John
Stevens, Hewlett & Perkins
1 Serjeants' Inn
Fleet Street
London EC4Y 1LL (GB)

(71) Applicant: JAPAN EXLAN COMPANY, LTD.
Osaka-shi Osaka 530 (JP)

(72) Inventors:

• Tanaka, Koji
Okayama-shi, Okayama-ken (JP)

(54) High moisture adsorptive and desorptive fine particles and process for producing the same

(57) Fine particles (having a particle diameter smaller than 10 µm) of crosslinked acrylonitrile polymer capable of absorbing and releasing a large amount of moisture, in which the acrylonitrile polymer is crosslinked with hydrazine such that the nitrogen content increases by 1.0-15.0 wt% and there being introduced salt type carboxyl groups in an amount of 1.0 mmol/g or more into a part of the remaining nitrile

groups. Said fine particles are prepared by treating an emulsion of acrylonitrile polymer with hydrazine so that crosslinks are formed in the acrylonitrile polymer and the nitrogen content increases by 1.0-15.0 wt% and then hydrolyzing the crosslinked acrylonitrile polymer so as to introduce more than 1.0 mmol/g of carboxyl groups in salt form into nitrile groups remaining uncrosslinked and to introduce amide groups to the rest of nitrile groups.

EP 0 716 882 A1

Description**BACKGROUND OF THE INVENTION**

5 1. Field of the Invention:

The present invention relates to moisture adsorptive and desorptive fine particles which perform moisture adsorption and desorption reversibly and withstand repeated use.

10 2. Description of the Prior Art:

A conventional way of removing moisture from air resorts to moisture absorbents such as lithium chloride, calcium chloride, magnesium chloride, and phosphorus pentoxide. Despite their ability to absorb a large amount of moisture rapidly, they possess some drawbacks due to their deliquescence. That is, they become liquid after moisture absorption, causing contamination, and they are difficult to mold and regenerate. Other moisture absorbents such as silica gel, zeolite, sodium sulfate, activated alumina, and activated carbon suffer the disadvantage of being limited in the amount of moisture absorption, being slow in the rate of moisture absorption, and requiring high temperature for their regeneration. This prevents them from being put to practical use. These moisture absorbents pose a problem when used as an additive. That is, they impair the physical properties and appearance of the material to which they are added, because they have a large particle size.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide high moisture adsorptive and desorptive fine particles and a process for producing the same. This moisture absorbent absorbs a large amount of moisture, can be regenerated easily by drying, and has such a small particle diameter that it does not impair the appearance and physical properties of the base material when used as an additive.

The above-mentioned object of the present invention can be achieved by high moisture adsorptive and desorptive fine particles characterized in that said particles are of crosslinked acrylonitrile polymer and are 1.0-15.0% by weight of the increase in nitrogen content due to crosslinking by hydrazine, there being introduced salt type carboxyl groups in an amount of 1.0 mmol/g or more into a part of the remaining nitrile groups, and the particle diameter of said fine particles being 10 µm or less.

The above-mentioned object of the present invention can also be achieved by a process for producing high moisture adsorptive and desorptive fine particles characterized in that an emulsion of an acrylonitrile polymer is subjected to the treatment with hydrazine to introduce crosslinking bond into the fine particles so that the increase in the nitrogen content is 1.0-15.0% by weight, and then subjected to hydrolysis so that there are introduced carboxyl groups into 1.0 mmol/g or more of the remaining nitrile groups and amide groups are introduced into all of the remaining nitrile groups, said carboxyl groups being in the form of salt type.

40 **DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The product according to the present invention is in the form of fine particles of crosslinked acrylonitrile polymer. It is produced from fine particles of acrylonitrile polymer containing more than 40 wt%, preferably more than 50 wt%, of acrylonitrile (AN for short hereinafter). The AN polymer may be either a homopolymer or a copolymer with a comonomer. Examples of the comonomer include vinyl halide and vinylidene halide; (meth)acrylic ester; sulfonic acid-containing monomer and salt thereof (such as methlysulfonic acid and p-styrenesulfonic acid and the like); carboxylic acid-containing monomer and salt thereof (such as (meth)acrylic acid and itaconic acid and the like); and acrylamide, styrene, and vinyl acetate and the like. The AN polymer fine particles as the starting material can be prepared typically by the process disclosed in Japanese Patent Publication No. 2207/1980. The present invention is not limited to this process.

The method of introducing hydrazine crosslinks (crosslinking) into the AN polymer fine particles is not specifically limited so long as it is capable of increasing the nitrogen content by 1.0-15.0 wt%. An industrially favorable method is treatment at 50-120°C for 0.5-5 hours in the form of emulsion containing 6-80% of hydrazine. "Increase in nitrogen content" means the difference between the nitrogen content (in wt% based on fine particles) in AN polymer fine particles as the starting material and the nitrogen content (in wt% based on fine particles) in hydrazine-crosslinked AN polymer fine particles. If the increase in nitrogen content is less than the lower limit specified above, the fine particles will dissolve in water in the subsequent step of hydrolysis which is intended to introduce carboxyl groups, and hence the object of the present invention is not achieved. If the increase in nitrogen content exceeds the upper limit specified above, the

fine particles do not accept more than 1.0 mmol/g of carboxyl groups in the subsequent step, and hence the object of the present invention is not achieved. The condition under which the nitrogen content increases by 1.0-15.0 wt% will vary depending on the reaction temperature and time and the concentrations of reactants which may be determined easily by experiment. Examples of the hydrazine include hydrazine hydrate, hydrazine sulfate, hydrazine hydrochloride, hydrazine nitrate, and hydrazine hydrobromide and the like.

According to the process of the present invention, nitrile groups remaining intact after crosslinking by hydrazine are substantially eliminated by hydrolysis in such a manner that more than 1.0 mmol/g of carboxyl groups in salt form are introduced into nitrile groups and amide groups are introduced into the rest of nitrile groups. This process is accomplished by heat treatment in the presence of an alkaline aqueous solution of alkali metal hydroxide or ammonia or a mineral acid such as nitric acid, sulfuric acid, and hydrochloric acid and the like. According to the present invention, the amount of carboxyl groups in salt form should be more than 1.0 mmol/g. This condition may be easily determined by experiment on the relation between the amount of carboxyl groups in salt form and the reaction factors (such as temperature, concentration, and time). Incidentally, it is also possible to carry out hydrolysis simultaneously with the introduction of crosslinks. In the case where an acid is used for hydrolysis, it is necessary to convert the carboxyl groups into those of salt form.

An adequate method of converting carboxyl groups into those of salt form is to treat the hydrolyzed emulsion with any of hydroxides of a variety of salt types or salts exemplified below. Salts of carboxyl groups are formed from cationic ion of alkali metals (such as Li, Na, and K and the like), alkaline earth metals (such as Be, Mg, Ca, and Ba and the like), other metals (such as Cu, Zn, Al, Mn, Ag, Fe, Co., and Ni and the like), NH₄, and organic (such as amine and the like). If the amount of carboxyl groups in salt form is less than the lower limit specified above, the resulting product does not exhibit the desired performance. More than one salt may be used.

According to the present invention, the fine particles should have a particle diameter smaller than 10 µm. The way of achieving this object is not specifically limited. A typical example is disclosed in Japanese Patent Publication No. 2207/1980. A particle diameter greater than 10 µm leads to a slow rate of moisture absorption. Such fine particles impair the appearance and physical properties of the base material and easily drop off from the base material when used as an additive.

In this way it is possible to provide the fine particles mentioned above which have a moisture absorption higher than 20%, preferably higher than 35% and which can be easily regenerated by drying. Moisture absorption is measured by the method described in Example which follows.

It is not yet fully elucidated why the fine particles of the present invention have the high moisture adsorptive and desorative properties. A probable reason is as follows: The fact that the fine particles contain substantially no nitrile groups although they are prepared from AN polymer suggests that side chains attached to polymer chains have the crosslink structure containing nitrogen which is formed by reaction with hydrazine and the carboxyl groups in salt form which are formed by hydrolysis of nitrile groups. In addition, it is considered that the crosslinking structure also contributes to moisture absorption judging from the fact that the carboxyl groups in salt form are not enough in quantity for high moisture absorption although they are capable of absorbing and releasing moisture. Moreover, the fact that the fine particles after moisture absorption are not sticky suggests a high degree of crosslinking.

The invention will be described with reference to the following examples, in which parts and percent are based on weight unless otherwise indicated.

The amount (mmol/g) of carboxyl groups in salt form and the moisture absorption were measured according to the following procedure.

(1) Amount (mmol/g) of carboxyl groups in salt form:

Accurately weigh about 1 g of completely dried sample. Add 200 g of water to the weighed sample. After heating to 50°C, add 1-N hydrochloric acid to adjust the solution to pH 2. Titration curve was obtained with 0.1-N NaOH solution in the usual way. From the titration curve, an amount of NaOH solution which was consumed by carboxyl groups was obtained. The amount of carboxyl groups is calculated from the equation below.

$$\text{Amount of carboxyl groups} = (0.1 \times Y) / X$$

where X is the amount (g) of sample, and Y is the volume (cc) of NaOH solution which was consumed by carboxyl groups.

Repeat the same procedure as above, excluding the pH adjustment. The amount of carboxyl groups in salt form is calculated from the equation below.

55

$$(\text{Amount of carboxyl groups in salt form}) =$$

$$(\text{Amount of carboxyl groups}) - (\text{Amount of carboxylic acid})$$

(2) Moisture absorption (%)